# Thermal Energy of Mixtures II

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We have found that conservation of Internal Energy, hence upholding the first law of thermodynamics, obliges us to include *configurational entropy* in Internal Energy.
We recall:

$$U = U_{mic} - TS_{conf} \qquad (\text{generally } U = U_{mic} - \int dT S_{conf}(T) )$$

Heat capacity becomes $\qquad C_V = C_{Vmic} - S_{conf}$

$U_{mic}$ is the microscopic Internal Energy, $S_{conf}$ is the configurational entropy of the mixture.
For pure substances, $S_{conf} = 0$ and there is no contribution.

How come we got the right result in osmosis without this modification of Internal Energy?
In osmosis, the pressure difference was obtained by equating water chemical potential on each side of a semi-permeable membrane (spm). This ensures first-order stationarity of Gibbs potential upon bringing particles from one side of the spm to the other (dG = 0).
If, however, we plug our new expression for Internal Energy in, we somehow "double up" the entropy effect arriving at a glaring contradiction. So, our original reasoning must have been wrong.

Change of Gibbs potential is $\qquad dG = -SdT + Vdp$

There is a pressure change across the spm. When we apply the usual reasoning of (water) particles going to and fro across the spm, we can *feel entitled* to a difference in chemical potential as

$$\Delta\mu_w = v_w \, \Delta p$$

This cancels the pressure term in the expression for the chemical potential, leaving

$$\Delta u - T\Delta s = 0$$

This directly gives us the modification of Internal Energy (but changes G).
In order to get the pressure difference back, we postulate that an energy gradient exerts a force which must be counterbalanced by a pressure gradient to give zero current, hence

$$\Delta u = T\Delta s = v_w \, \Delta p$$

This derivation is, admittedly, quite involved and handwaving calling for an experimental test.
It could be the measurement of specific heat as a function of configurational entropy, species concentration that is to say, under conditions excluding any parasitic effects.
We have such conditions when mixing *isotopes* of one single species.
Practically, take molten metal of two isotopes and measure specific heat vs isotope proportion.
Choose isotopes of same nuclear spin to avoid quantum statistical issues.
We should get a minimum of specific heat at equal isotope content.

Now that we are done with the nitty-gritty, let us point out that in this year 2024AD, after 200 years of thermodynamics and 150 years of Boltzmann's definition of entropy, we have, on top of kinetic and interaction energy, discovered a new, third, form of energy - *configurational energy*.